In Situ Synthesis of TiB_2/NiAl Composite

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Abstract. In situ synthesis technology was used to synthesize the NiAl matrix composite reinforced by TiB_2 which were fabricated by induction heating furnace in this work. Modern testing technologies were applied to analyze the microstructures of the products and the reaction process. The results showed that the composite consisted of NiAl and TiB_2 phases. The ignition temperatures of Ni+Al→NiAl and Ti+2B→TiB_2 were approximately 626°C and 1029°C when heating in 20K/min. The activation energy of above reactions were $295.86\,\mathrm{k}J/\mathrm{mol}$ and $113.08\,\mathrm{k}J/\mathrm{mol}$, respectively. TiB_2 phase with fine particle was uniformly distributed in the NiAl matrix in the form of hexagonal prism.

Introduction

NiAl inter-metallic compounds are a new type of high-temperature structural materials which possess high melting point, low density, high thermal conductivity and excellent oxidation resistance along with some other characteristics, therefore, they are widely used in the aerospace and military industry[1,2].

In situ synthesis is a new method for preparing composite materials which have recently developed. The basic principle is to rely on alloy composition design. Using in situ synthesis in different elements or substances, chemical reactions will take place, and in the metal matrix, it can generate one, even several kinds of high hardness, and high elastic modulus of ceramic or inter-metallic compound as the reinforcing phase to improve the performance of a single metal alloy. The enhanced phase thermodynamically driven by in situ reaction is stable, the distribution is relatively uniform; the reinforced phase and matrix of the coherent is good, the interface with high bonding strength is clear. So compared with matrix metal, composite material has better mechanical properties at both room and high temperature. In this experiment, we use the thermal explosion reaction technology to in situ synthesize the NiAl matrix composite from Ni-Al-Ti-B system, explore the process and product of the composite materials, thus, provide a new direction for the preparation of the NiAl inter-metallic compounds[3-7].

Experiment Procedures

Raw materials of this experiment were titanium powder (3-5μm, 99% purity), aluminum powder (3-50μm, 99% purity), nickel powder (10~30μm, 99.8% purity) and boron powder (3-10μm, 99% purity). Produce NiAl-based composites with reinforcement volume fraction of 20% (i.e. 20vol. % TiB2 + 80 vol. % NiAl), the powder mixture of Al, Ti, B and Ni were prepared with their respective volume fractions derived from the reaction equation Ti+2B+Ni+ Al→TiB_2+NiAl. The weight ratio of Al, Ti, B and Ni in the mixed powder is thus 17.55%; 16.96%; 7.64 %; 57.85% (in wt. %). The powder mix was first ball-milled in a stainless steel vacuum jar for 4h and then compacted under a pressure of 180MPa into cylindrical specimens with a diameter of 20mm and height about 5mm. The cylindrical specimens were first placed in a vacuum jar and an induction heating furnace. The temperature of the compact was measured by a thermal couple and plotted as a function of heating time. After reaction, the furnace was turned off and cooled down to room temperature. And the composite samples were mechanically polished and investigated by using X-ray diffraction (XRD, RigakuD/MAX2400), and scanning electron microscopy (SEM, Quanta 2000). In order to obtain the differential scanning calorimetry (DSC, Netzsch STA449C) curves, the compact samples were heated in argon atmosphere in the furnace of STA449C thermal analyzer, wherein the temperature was increased from the ambient (20°C) to 1150°C at different heating rate such as 10k/min; 15k/min; 20k/min; 25k/min. The reactions occurring in the Ni-Al-Ti-B system during the heating process were analyzed.

Results and Discussion

Thermodynamics Calculation

According to common Gibbs-Heimalmholtz approximate calculation equation[8]:

$$\Delta G_T^{\theta} = \Delta H_{298}^{\theta} - T\Delta S_{298}^{\theta} \tag{1}$$

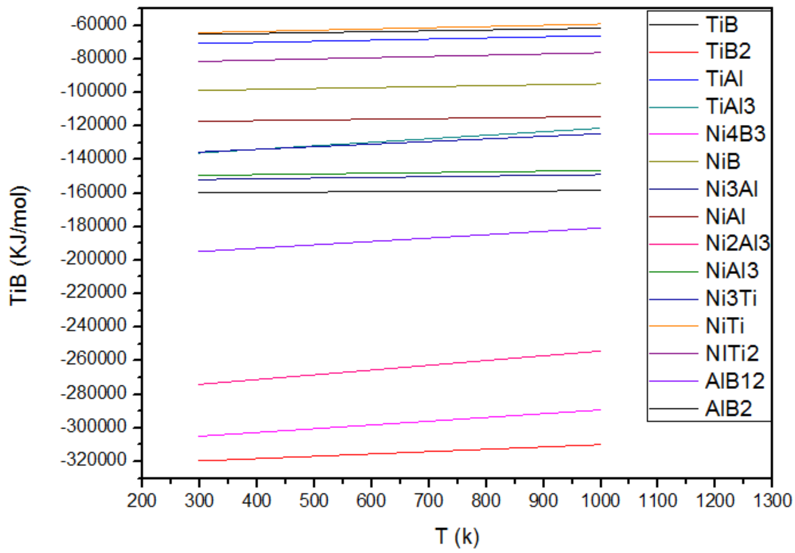


Fig.1 Curves of Free Energy

Figure 1 showed the Gibbs function relation expression of the 15 products which may exist in the reaction referring to the practical inorganic thermodynamics data. Based on the figure 1 all the values of the function relations were negative meaning that the reactions can take place spontaneously in terms of thermodynamics.

DSC Analysis

Figure 2 showed the DSC curves of different system and different heating rates. Figure 2 (a) showed the DSC superposition curve of Ni-Al, Ni-B, Ni-Ti, Ti-B, Ti-Al and Al-B; (b) showed the DSC curve of Ni-Al-Ti-B; (c) showed the DSC curve of different heating rates. From Figure 2 (a), it can be concluded that the reaction sequence of four elements Ni, Al, Ti, B as follow: Al and B reacted at 659°C, Ni and Al at 550°C, Ni and B at 588°C, Ti and Al at 665°C. Ti and B at 1080°C, Ni and Ti at 1109°C. According to the curve of Gibbs free energy (Figure 1), the reaction $Ti + 2B \rightarrow TiB_2$ has the minimum free energy function value meaning it was the most likely reaction in each of the six reactions. Meanwhile, it corresponded to the second exothermic peak (1080°C) in Figure 2 (b). The reaction of Ni-Al corresponded to the first exothermic peak (633°C) in Figure 2 (b). From figure 2 (c), it showed the DSC curves with heating rate of 10K/min, 15K/min, 20K/min and 25K/min. Peak A represented the reaction: Ni+Al→NiAl and peak B represented the reaction: $Ti+2B \rightarrow TiB_2$. Four different heating rates of DSC curves emerged exothermic peak A between 633°C and 635°C. While the exothermic peak B appeared at a temperature ranging from 1023°C to 1080°C. The law is that the endothermic peak will move to the high temperature zone if the heating rate was raised.

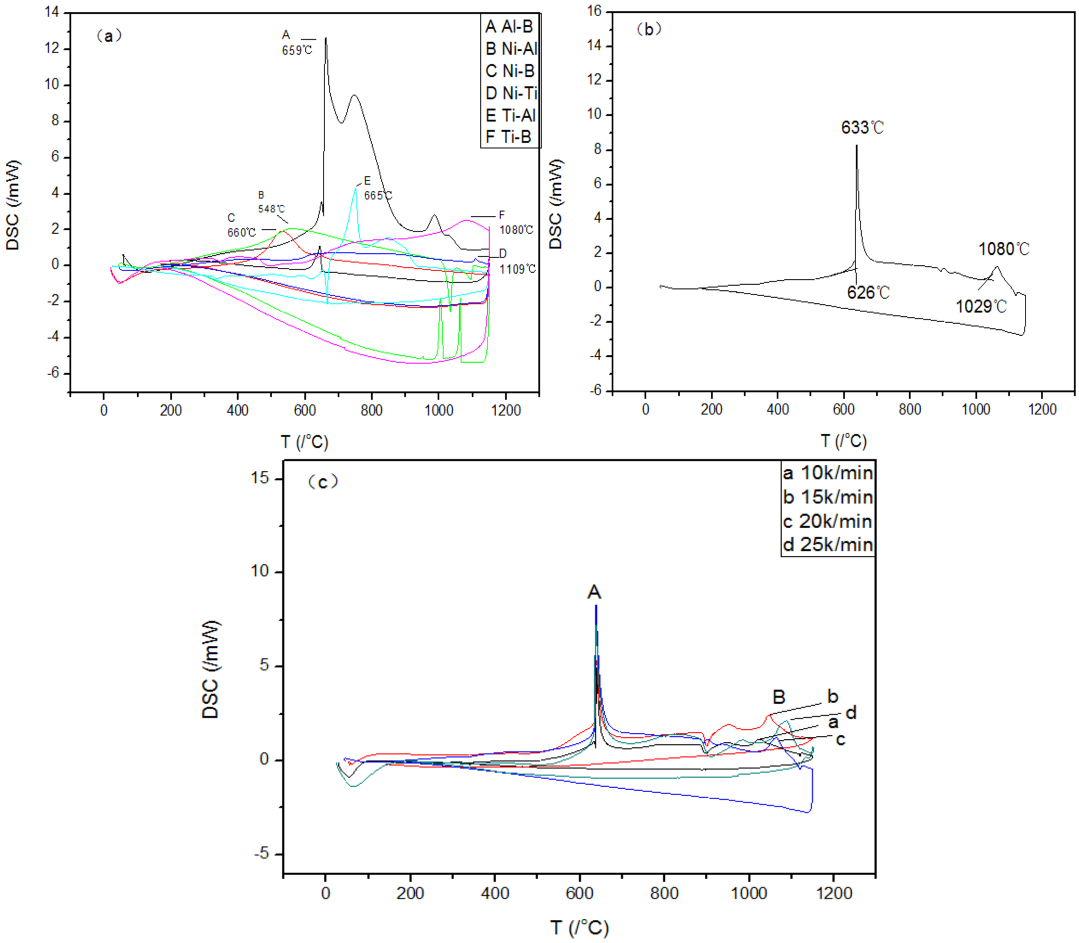


Fig.2 (a) DSC Superposition Curves of Ni-Al, Ni-B, Ni-Ti, Ti-B, Ti-Al, Al-B (b) DSC Curve of Ni-Al-Ti-B (c) DSC Curves of Different Heating Rates of 10K/min, 15K/min, 20K/min and 25K/min

According to the Kissinger equation[9]:

$$-E/R = \frac{\mathrm{d}\ln\frac{\beta}{T_m^2}}{\mathrm{d}\frac{1}{T_m}} \tag{2}$$

Figure 3 showed the regression curves of reaction A and reaction B (Figure 2 (c)). The activation energy can be calculated using the equation above. As it was shown in Figure 3 the slope of the regression line was the activation energy. According to Figure 3 (a) and (b), the activation energy of reaction A can be calculated: $E_{(A)} = 295.86\,kJ/\mathrm{mol}$. The activation energy of reaction B: $E_{(B)} = 113.08\,kJ/\mathrm{mol}$.

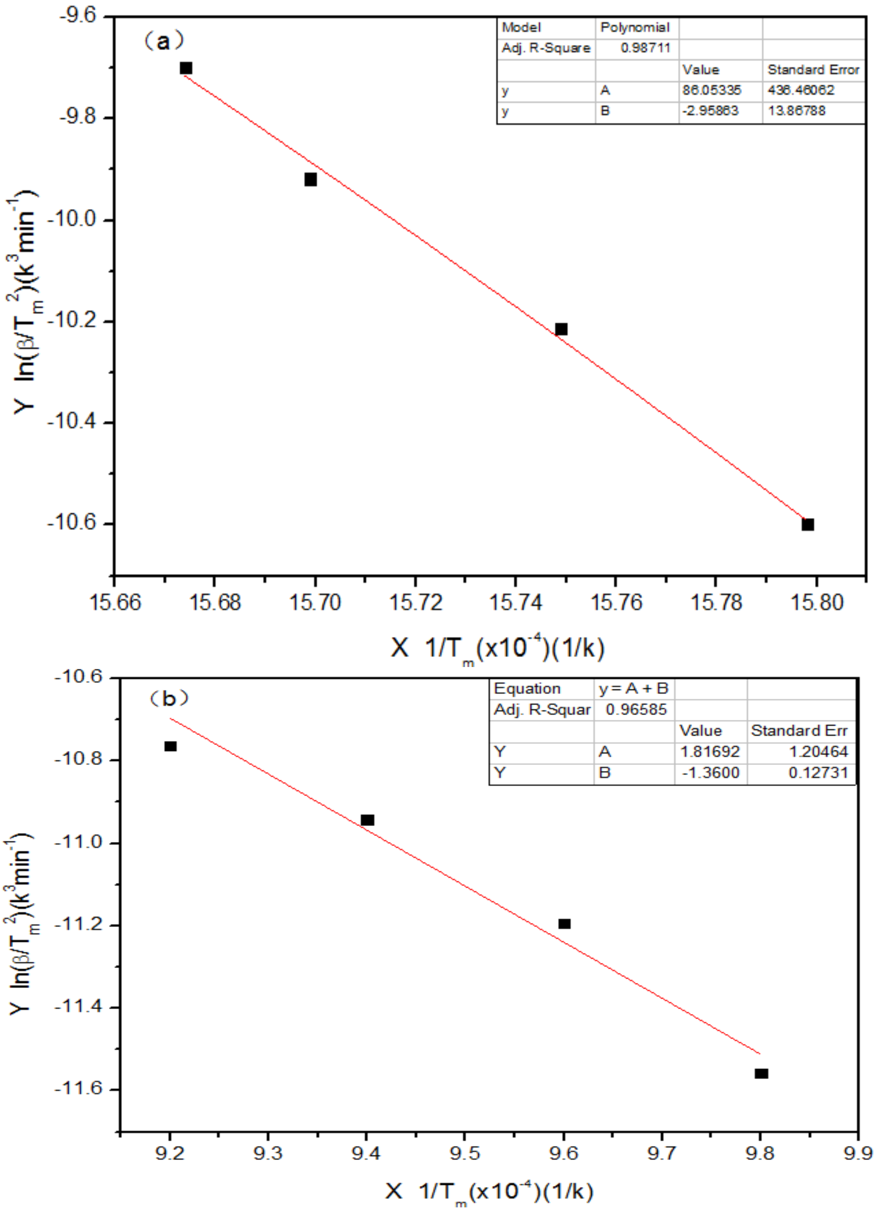
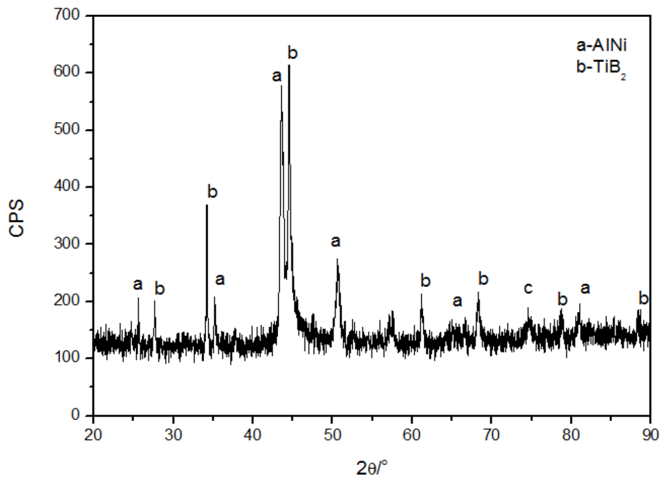


Fig.3 (a) The Regression Curve of Point A (b) The Regression Curve of Point B

X-Ray Diffraction and Morphology Analysis



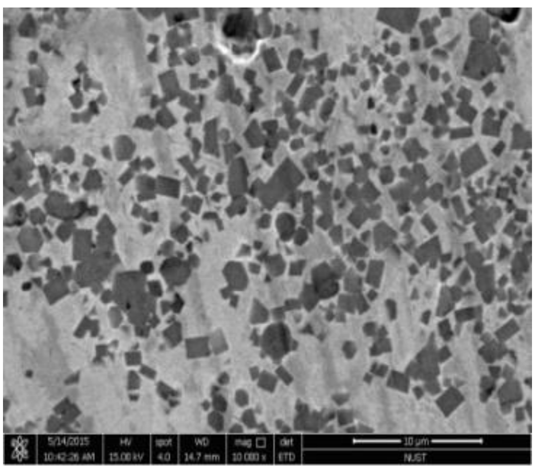


Fig.4 Diffraction Diagram of the Sample Fig.5 SEM Photograph of the Sample

Figure 4 showed the diffraction diagram of the composite and figure 5 was the SEM photograph of the composite. It can be seen from Figure 4, that the sample was mainly NiAl and TiB_2 phases. The matrix of this composite was NiAl and TiB_2 was the reinforcement.

In the SEM photograph (Figure 5) the rectangle and hexagon area was the TiB_2 phase surrounded by the matrix constituent by NiAl phase. The TiB_2 phases with fine particles were distributed uniformly in the matrix in the form of hexagonal prism through the photograph.

Summary

(1) The composite was constituent by matrix NiAl and reinforcement TiB_2. The fine particle TiB_2 in the form of hexagonal prism was distributed uniformly in the matrix.

(2) The ignition temperature of Ni+Al→NiAl and Ti+2B→TiB_2 were 626°C and 1029°C. The activation energy of the above reactions were $295.86 kJ/\mathrm{mol}$ and $113.08 kJ/\mathrm{mol}$.

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